Nitrogen-containing carbon catalyst for use in PEM fuel cell cathodes

Honors Thesis for Graduation with Distinction

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Abstract

Fuel cells are an alternative energy source to traditional energy sources, such as combustion engines or batteries. They create energy through the electrochemical reaction between hydrogen and oxygen, leaving water as a byproduct. Therefore as an energy source, fuel cells are very clean, effective, and environmentally friendly, making them advantageous in the long run when compared with most traditional energy sources. There are many classes of fuel cells, but low temperature PEM fuel cells are especially important because they are used in transportation and automotive industries. Although fuel cells have many advantages, they are not c urrently cost effective to produce. This research explores the creation and implementation of alternative materials that are cheaper, and have better active and conductive properties which will help improve the performance of fuel cells, and make them available for application in daily life. During this study, composites of highly active (but less conductive) and highly conductive (but less active) catalyst were determined to be useful for the making of better materials. The best composite found was one that contained 25% active fibers and a secondary conductive catalyst. In addition, Fe and Co supported by SiO_2 or MgO had high activity and better conductivity than fibers grown from Fe supported by Al_2O_3 in some cases. No methanol oxidation activity was observed, this is a positive result for methanol fuel cells since methanol would not react with the materials used in the fuel cell. Separation techniques and full fuel cells were studied as well.

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1. Introduction

Fuel cells are electrochemical energy conversion devices. Hydrogen and oxygen are reacted producing electricity and forming water. The development of Fuel Cells is of great importance because they are powered by, hydrogen and oxygen, which are abundant on the earth, and are very environmentally friendly. Currently, hydrogen production is 48% from natural gas, 30% from oil, 18% from coal, and 4% from water electrolysis [6]

With limited amounts of worldwide natural resources, fuel cells, or another alternative energy sources, will someday be needed not only for environmental reasons, but necessary for developed economies to operate efficiently.

Proton Exchange Membrane (PEM) fuel cells are a very promising source of alternative energy and are being investigated for their use in transportation. These fuel cells are named by the electrolyte they employ; in this case is a solid polymer electrolyte.

Despite all the benefits fuel cells have, they have many problems preventing them from being commercialized. One major problem is due to the cathode they use, platinum. Platinum is used as a catalyst for the low temperature oxygen reduction reaction. Platinum, a precious metal, is expensive, has rather slow kinetics for oxygen reduction reaction and mass transfer effects that limits power.

The oxygen reduction reaction that occurs in the cathode is shown here:

$$O_{2(aq)} + 4H^+ + 4e^- \rightarrow 2H_2O \qquad (1)$$

Typically, carbon is used as a support for platinum to increase mass transfer properties and reduce platinum loadings. Carbon is a critical material used in fuel cells, since it can

have all the necessary conditions for electronic conductivity, corrosion resistance in acidic media, surface properties, and low cost. Previously, newly developed nitrogen containing carbon samples were active materials for the ORR without platinum but their conductivity was not good enough [11]. Looking at Figures 1 and 2 with example graphs of I-V curves and power curves, it is evident that less catalytically active samples have a larger initial voltage drop in region 1. This also shows that conductivity, which is the changing slope in region 2, effects power. More conductive samples have a less negative slope in this region. Mass transfer also effects power, dropping the voltage as well. Samples with better mass transfer will not reach the oxygen diffusion limiting current, or region 3, until a higher value. Lastly, since P=I*V, improvements in any region can improve the power.

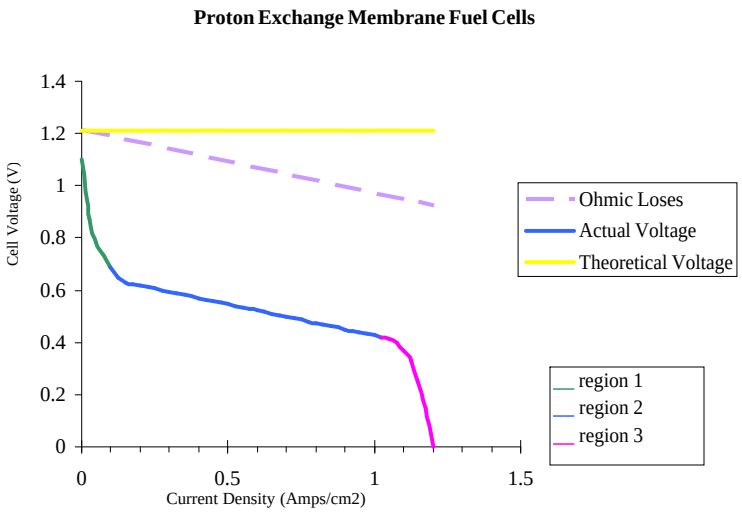


Figure 1. Proton Exchange Membrane Fuel Cells

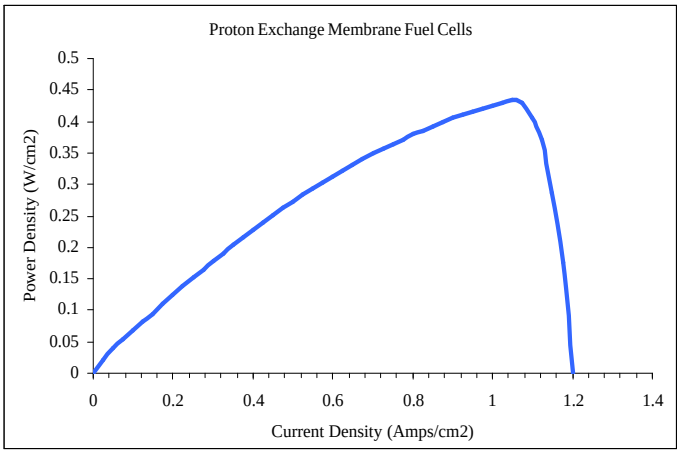


Figure 2. Proton Exchange Membrane Fuel Cell

The carbon materials that have been developed are carbon nanofibers containing nitrogen to improve activity. However, these carbon nanofibers have some limitations such as low production, and low conductivity. This project focuses in the development of active catalysts from metal, carbon and nitrogen. One of the metals used for the making of catalyst is iron. Iron is a catalyst that allows the formation of active sites by increasing the number of carbon edge planes exposed, and increasing the kinetics. The carbon structure of the alternative supports has an effect on the edge plane exposure. There are four different types of nanofibers: multi-walled nano-tubes, onion like fibers, stacked platelets, and stacked cups [11]. The stacked platelets will have the most exposure because of the edge planes and therefore increase the activity of the sample when reacting with oxygen, while the multi-walled nano-tubes will have less edge exposure but more basal plane exposure, increasing the conductivity of the catalyst. This catalyst will serve as the cathode backing for the fuel cells. Figure 3 shows the fibers diagram.

The exposed edge planes chemisorb oxygen and with this increased interaction with oxygen the activity increases. There are different nanostructures formed in different catalysts from iron and nickel.

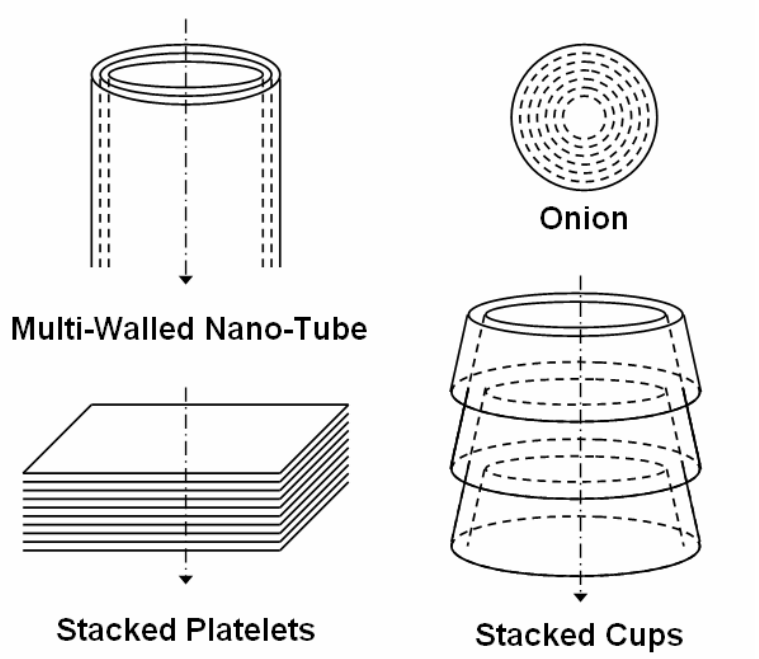


Figure 3. Alternative Supports [10]

The aim of this project was to obtain a catalyst that is very conductive with some of the more active samples and see if this new sample has better performance with respect to conductivity, activity and mass transfer. There are samples that were found to have combined nanofiber structures that will favor activity as well as conductivity of the samples. The samples created are tested and, depending on the results, considered as an alternate cathode that could be more efficient than platinum.

Testing is done using different methods. For conductivity a potentiostat is used, and for activity a Rotating Disk Electrode (RDE) half cell connected to a potentiostat is used. For characterization TEM and separation methods are used. To determine the different types of carbon used in the catalyst a hydrophobicity test using organic extraction is used. A newly developed material would hopefully be cheaper, more

conductive, and more active and with less mass transfer affects than platinum, enhancing the power of the fuel cells.

2. Literature Review

PEM fuel cells have become of great interest for transportation applications for their environmental friendliness, high energy density, low operating temperature, low emissions, and minimal corrosion properties [3]. However, PEMFC are not very commercially viable because of their expensive manufacturing cost. Platinum is the electrocatalyst used for oxygen reduction in the fuel cell. Platinum is very expensive and of limited supply. For this reason, research has been focusing on creating new catalytic sites and carbon support simultaneously. Preparation of nitrogen containing precursors with iron could replace the usage of platinum in the making of fuel cells.

2.1 Nitrogen-containing carbon

According to *Gojkovic et. Al.* one method to develop new catalyst is with nitric acid and ammonia treatments of carbon which is an effective way to introduce nitrogen containing groups on the surface of the carbon. These nitrogen groups will help the catalyst to have more active sites, and therefore improve the catalyst's activity.
Recently it has been discovered that active electrodes could be prepared by heat-treating metal and nitrogen precursors together in the presence of the carbon support.

Carbon nanofibers are being grown with heat treatment that has optimal effects on activity from silica or magnesia support and metals such as Iron, Cobalt or Nickel. The oxygen reduction rate will increase with temperature of the catalyst. During the heat treatment the chelates migrate over to a carbon support and forms active sites [5]. Though there is an amount of iron where activity levels off and then decreases. This last method has improved electrocatalytic activity, because of the presence of edge planes in the carbon nanofibers.

2.2 Fuel Cell Preparation

Membrane Electrode Assembly Fuel Cells are made of five different layers. An anode Flowfield, the anode backing gas diffusion layer, a catalyst coated membrane, a cathode backing gas diffusion layer, and finally the cathode flowfield. Figure 4 shows the diagram of a MEA fuel cell. MEA fuel cells, however, have several manufacturing issues such as cracking, delamination, thickness variation, composition variations, and macroscopic orientations. Cracking causes catalytic inactivity, increases resistance of the catalyst layer, catalytic erosion. Delamination causes resistance between the layers, flooded areas, and imbalance in current and ion flow. Thickness variations cause crossover, shorting, mechanical weak spots and pinholes. Composition variations cause increase resistance to ion transport, reduction of activity areas, and hot/cold spots. Last, macroscopic orientations cause resistance variations, mechanical stress variations, and less control in morphology [8]

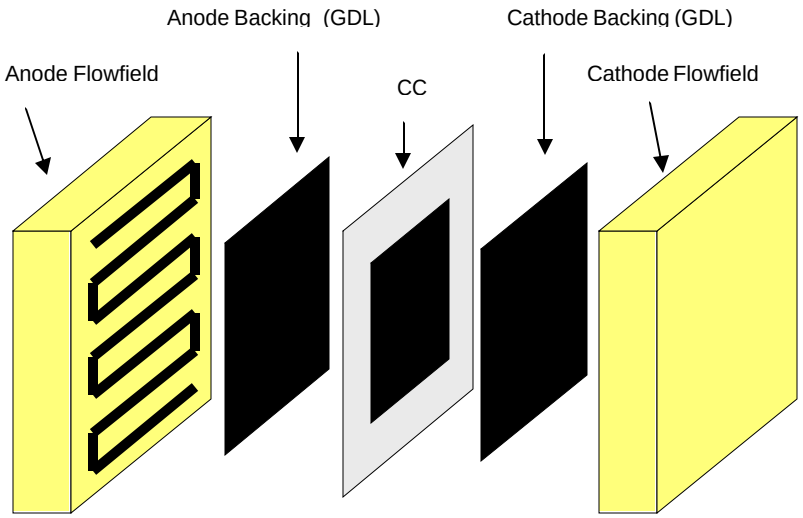


Figure 4. Five layer MEA Fuel Cell [10].

Los Alamos National Laboratory has developed different methods of MEA fuel cell making. Their fabrication method of Hydrogen MEA Fuel Cell is first making the carbon supported catalyst, then paint and oven dry decals, clean and cation exchange PEM to Na^+ form, dry on heated vacuum table for hot pressing, hot press decals onto the PEM, cation exchange PEM with electrodes to H^+ form, and finally insert PEM with electrodes and gas diffusion layers, the MEA, into the fuel cell hardware for testing [2]. The procedure described above is about the same procedure that was used during this research. Refer to section 3.7 for more information.

Finally, Fuel cell characterization is done with potential sweep methods. The fuel cell is tested in a galvanic cell that converts chemical energy into electrical energy. These electrochemical methods help to predict the charge transfer kinetics, the results show that there is a limit potential drop as the current increases, and also that equilibrium is determined by thermodynamics, and the kinetics are influenced by the catalysts.

3. Experimental Methods

3.1 Fiber preparation.

Active fibers for the ORR were prepared by acetonitrile pyrolysis over supported Fe, Co, and Ni particles. The fibers were purified typically by washing the pyrolysis product with a strong acid. Details are presented elsewhere [11].

3.2 Catalyst Ink Preparation

The preparation of catalyst ink was made in the laboratory. A 1:1:10 ratio of catalyst, 5-wt% Nafion in aliphatic alcohols and ethanol were put into a small vial. Generally 10 mg of catalyst, 10 mg of Nafion, and 100 mg of ethanol were used. A black, clumpy solution was formed. The solution then was sonicated for twenty to thirty minutes to avoid any clumps of catalyst, and to obtain a very uniform solution. This ink was then used to test for activity, and conductivity of the catalyst.

3.3 Activity Testing

Activity testing was conducted using a RRDE using cyclic voltammetry (CV) experiments with a PAR 263A potentiostat/galvanostat with a 616 RRDE setup. A drop of catalyst ink approximately 10 micro liters was placed on the glassy carbon tip of the RRDE and allowed to dry. It covered all of the glassy carbon. The RRDE then was submerged into a 0.5 M solution of H_2SO_4 which was used as the electrolyte. The solution was then purged with oxygen for about 20 minutes, and an initial test sweep from 1.2 to 0 V (vs. NHE) at 10 mV/s was performed in order to remove gaseous oxygen from the pores and fill the pores of the catalyst with solution. This test sweep also allowed predicting what the activity of the catalyst would be. Then, the solution was purged with argon for 30 minutes to remove oxygen from the solution. When the argon

had been purged, five consecutive CVs were run from 0 to 1.2 to 0 V (vs. NHE) at 50 mV/s to obtain a baseline with of argon was obtained with a sweep from 1.2 to 0 to 1.2 V (vs. NHE) at 10 mV/s. Once the baseline had been obtained, the solution was then saturated with oxygen until consecutive CVs were the same. These CVs were run from 0 to 1.2 to 0 V at 50 mV/s and a slow CV at 10mV/s was obtained at different rotations from 0 to 2000 rpm. The glassy RDE was then cleaned with water and ethanol. Activity was measure by looking at the oxygen peak.

3.4 TEM

Phillips CM300 Ultra-Twin FEG and Phillips Tecnai TF20 instruments were used to perform TEM measurements. The catalyst was dispersed in excess ethanol, and sonicated for 30 minutes. A 200-mesh copper grid served as a support to Lacey-formvar carbon. Images and measurements are a courtesy of Paul Matter.

3.5 Conductivity Testing

Conductivity testing was performed on the catalyst ink prepared. The ink was placed evenly on three different copper plates covered with Teflon tape with a small hole punched in the middle. The holes were filled with catalyst, and the catalyst was dried. The small hole is the only part of copper exposed to the catalyst in order to measure the electrical resistance of the materials. After the ink dried, another copper plate was pressed against the catalyst with 100 psi of force to make electrical contact between the copper plate and the catalyst. The plates were connected to a PAR 263A potentiostat, and a voltage swept was performed from 0 to -.1 V. The resistance obtained in the measurement was used to calculate the conductivity of the catalyst. The three different

plates accounted for three different replicates of experiments, and the average conductivity was taken to be the final value.

3.6 Hydrophobicity Testing

The hydrophobicity testing of the catalyst was performed using organic separation extraction. A catalyst sample, about 1 mg was put into a vial. Then, three pipet fulls, about 3 mg of hexane was added to the vial. The solution was then sonicated for about twenty minutes. About 6 ml of water were then added to the solution. The mixture was then shaken gently and a picture was then taken. As the solution separated, another vial was weighted. With a pipet, the top layer of the solution where some carbon was dispersed was extracted; care had to be taken to not extract the interface of the solution. Another picture of the solution, and the extract were taken. A second extraction was then performed adding 3 additional milliliters of hexane; the top layer was extracted from the solution were carbon was dispersed. Finally another picture was taken, and the extract, and the solution left in the vial were dried in the oven overnight.

3.7 Catalyst Ink Preparation and Application Method- MEA Fuel Cell

A catalyst ink was prepared by using 2.5:1:10 ratio of catalyst and 5-wt% Nafion in aliphatic alcohols, and ethanol. Generally 50 mg of catalyst, 200 mg of Nafion, and 2000 mg of ethanol were used. The ink solution was then sonicated for about 20 minutes in order to avoid any clumps, and to obtain a consistent solution. Glycerol was then added to the solution, the amount added was half the amount of nafion (about 100 mg) and the solution was then sonicated again for 30 minutes. A think coat of the well-mixed ink was then applied to one side of a 5 cm^2 of Teflon treated carbon cloth using a regular pipet. The ink had to be smooth, and there were no lumps formed on the cloth. The solution was

then dried, and another coat of ink was applied using the same procedure as stated above. This procedure was done until a smooth, uniform coat of catalyst was formed on the paper. The electrode was then dried for 24 to 48 hours. Then the electrode was dried in a furnace by ramping the temperature to 70 degrees Celsius, at 1 degree/min and holding for 1 hour.

The MEA fuel cell was then assembled by hot pressing the electrode together with a Nafion 115 membrane and a Nafion doped Pt anode using 1100 psi of force for 5 minutes at 130°C in between two plates containing some metal and not treated carbon paper. The fuel cell was ready for testing using a lab scale fuel cell stand.

3.8 Fuel Cell Testing

Fuel cell testing was done with a lab-scale PEM test stand for controlling testing conditions with online potentiostat for automated long-term activity testing. An open circuit voltage was obtained, and then the temperature and pressure of the fuel cell conditions were set. After the temperature and pressure stabilized, the test was conducted with the online potentiostat.

4. Results and Discussion

4.1 Catalyst Preparation

The catalysts used for the study of the Oxygen Reduction Reaction (ORR) were prepared by the pyrolysis of acetonitrile over various supports like Vulcan carbon, alumina, and silica, impregnated with Fe, Ni, or Co.

At an early stage of my research, Polymer composite preparation was done using active HF washed fibers grown from Fe/Al_2O_3 and PANI (13(~)/PANI). Three samples were made using 25wt%, 50wt%, and 75wt% fibers and the rest PANI. Testing for these samples is shown in the sections below.

Next, dual catalyst samples were prepared using active HF washed fibers grown from Fe/Al_2O_3 and a less active but more conductive secondary catalyst (9(M)/90(1)). These samples were tested for activity and conductivity having very promising results. Refer to sections below for more detailed results.

The next experiment done was using MeOH. This test was to see if there was any methanol oxidation in the sample. The tests were performed using active fibers 9(M), compared to commercial platinum samples, EC-20-PTC, and EC-20/10-Pt/Rv from Electrochem Inc.

MEA fuel cells were prepared using some of the dual catalyst samples (mixtures of active less conductive and more conductive but less active samples). For more information about this testing process please look in the section below.

Finally, hydrophobicity and TEM testing was done on the most promising carbon nanofibers in order to see if different types of carbon were composing the different

samples. The sections below describe each testing and the results obtained for the different catalyst samples made.

4.2 Activity Testing

Activity Testing is used to estimate the potential loss that will happen in a real fuel cell by a specific sample, and to extract kinetic information. Samples with optimal conductivity and catalytic activity are tested in a full lab-scale PEM fuel cell system.

The RDE has an electrolyte (0.5 M H_2SO_4) that gives out protons, which react at the cathode, acting like Nafion membrane that provides protons to the cathode in a PEM fuel cell. Oxygen in the electrolyte diffuses to the surface of the electrode reacting and forming water, and producing measurable current. The voltage is also controlled in the cathode giving a measure at which the reduction current increases. It can be seen that the oxygen is reacting from the difference in the reduction current for the oxygen saturated solution and the background current in the argon solution. The current peaks when the electrode is not rotating, this is caused by a temporary reaction of oxygen within the pores of the sample. The current is proportional to the area of the electrode so the electrochemically active area and current are initially very high, but when the reduction kinetics become very fast all the oxygen within the sample reacts, making the oxygen concentration zero at the front edge of the sample. Then the current becomes limited by the diffusion of oxygen from the bulk of the solution. So the kinetic current is greater when the reaction occurs in the pores than the mass transfer limited current under no rotation, because the pores provide higher surface area.

When the electrode is rotating, the mass transfer effects of oxygen diffusion and the pure kinetic current are present allowing for the measure of catalytic performance at specific

voltages. For more active materials, the peak voltage is higher.

Mass transfer current and the kinetic currents can be calculated using the following equations (2) and (3):

$$i_{mt} = nFAD_{OX}\left(\frac{\partial C_{OX}}{\partial y}\right)_{y=0} \quad (2)$$

where, i_{mt} is the mass transfer current, n is the moles or electrons, F is Faraday's constant, A is the electrode cross sectional area, D_{ox} is the diffusion of the oxidized species, C_{ox} is the concentration of the oxidized species, and y is the distance from the electrode's surface.

$$i_k = FAk(E)C_{OX}^b \quad (3)$$

where, i_k is the kinetics current, A is the electrode area including the pores, k (E) is the rate constant of the electrical potential/voltage, C_{ox}^{b} is the concentration of the oxidized species at the bulk. [1]

Activity for commercial samples is 750 mV, for vulcan carbon is 30 mV, and for active fibers is 650 mV. These activities are used for reference when determining catalytic activity of the samples prepared below.

Some samples tested for activity are summarized next. The polymer composites were tested for activity. As show in Figure 5, the activity peak shows that it is around 570 mV. NHE stands for Normal Hydrogen Electrode. Voltage always depends on what the reference is, in this case NHE is used as a reference in graphs since it is the other side in a fuel cell, but when voltage is measured in a half cell the reference is a Ag/AgCl electrode. Thus the voltage needs to be shifted by 200 mV since the Ag/AgCl is 200 mV less than

the NHE.

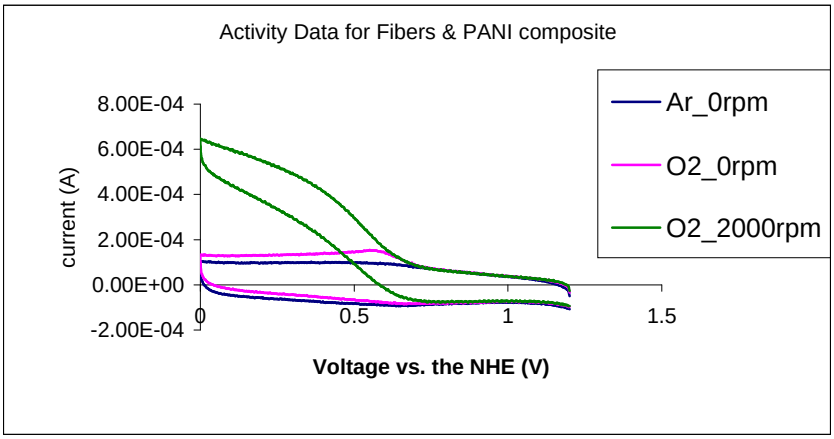


Figure 5. Activity Data for Fibers and PANI composites

The activity for dual catalyst composites was tested to see if they qualify for MEA fuel cell building. The dual catalyst is made by different amounts of nanofibers. As shown in Figure 6, the activity peak is at 636 mV for a composite with 25wt% active fibers. Figure 7 shows the activity for composites with 50wt% active fibers. The activity peak is this time at 622 mV. Composites with 75wt% fibers are shown in Figure 8, with an activity peak at 585 mV. Conductivity testing was also done with these samples as the following section will show.

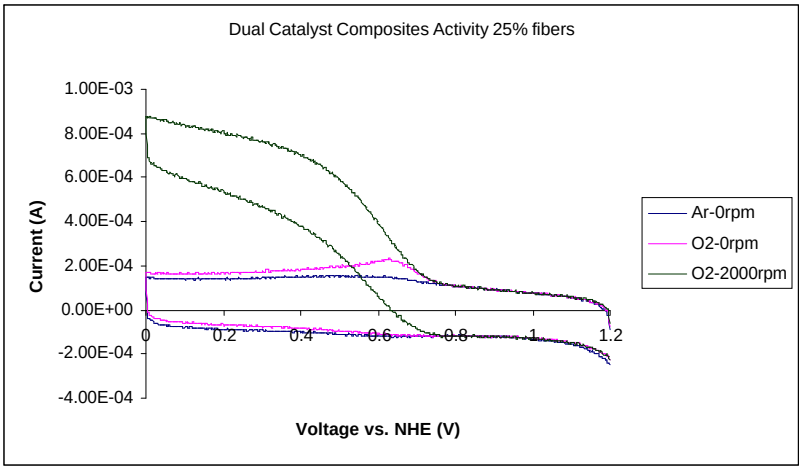


Figure 6. Dual Catalyst Composites Activity 25% fibers.

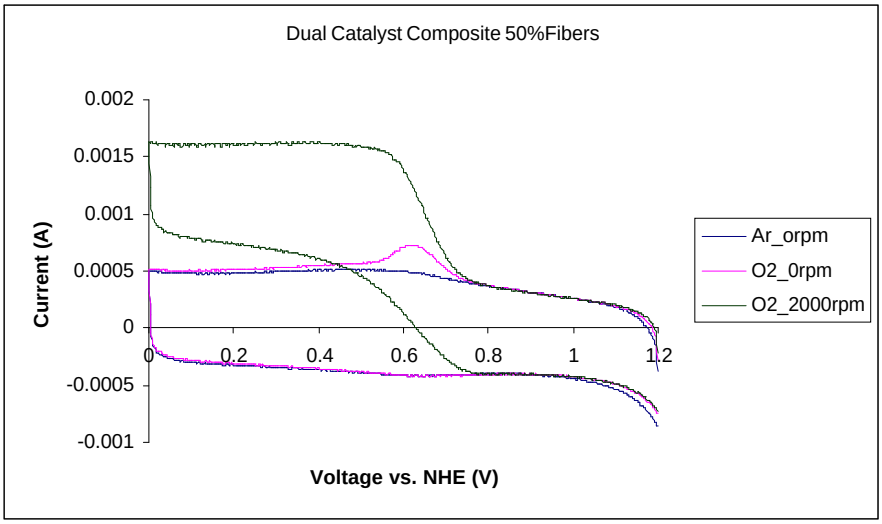


Figure 7. Dual Catalyst Composites Activity 50% fibers.

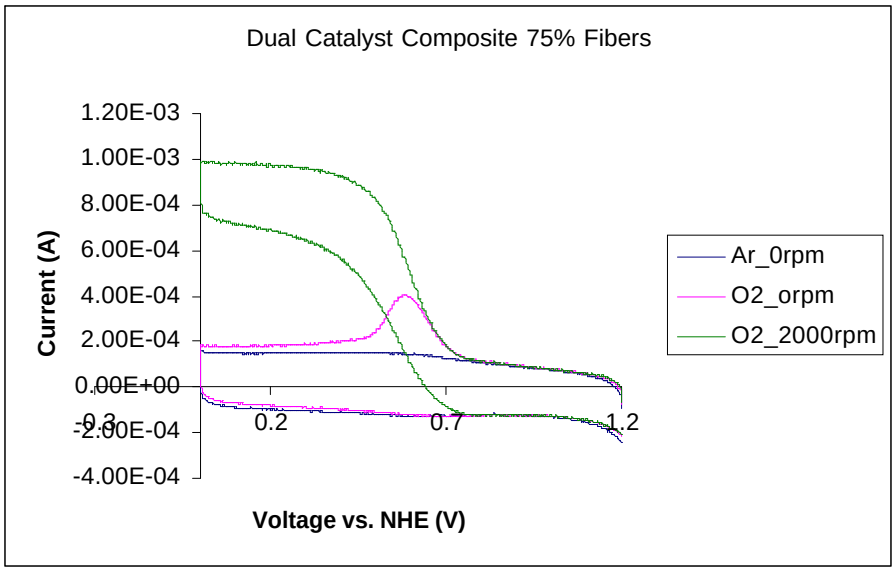


Figure 8. Dual Catalyst Composites Activity 75% fibers.

Activity measurements were taken with the electrode submerged in methanol solution, this was tested to see if methanol gets oxidized. Three tests were performed using dual catalyst containing fibers, as well as, using standard platinum catalyst. As Figure 9 shows, there is no activity or oxidation peak.

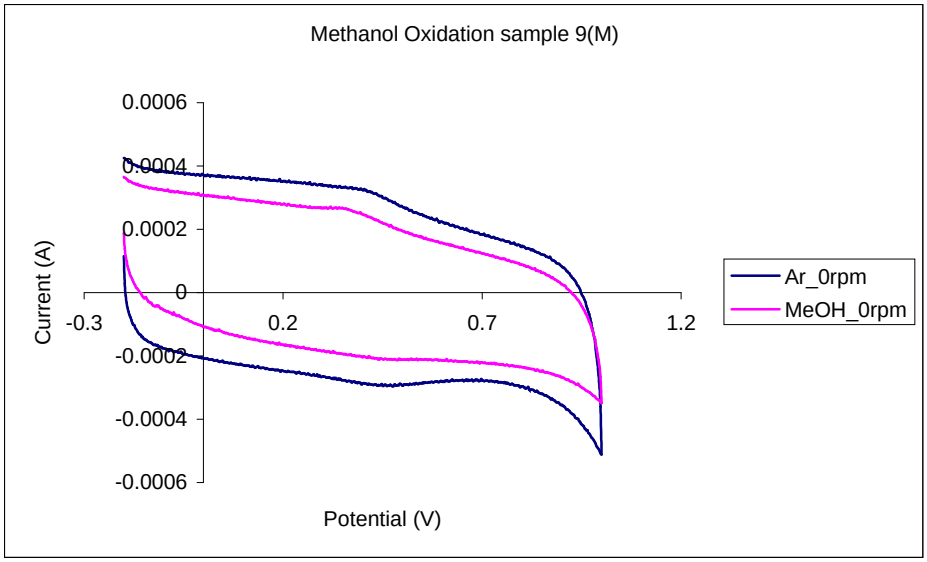


Figure 9. Methanol Oxidation Activity

Figure 10 shows the activity of commercial platinum when methanol is used, and when it is not. As seen in the Figures 10 and 11, the inverted peak shows an oxidation reaction when methanol is present for 2 different commercial catalysts (20-wt% Pt / VC, and a Pt/Ru alloy catalyst. This graph confirms the results obtained in the example above, where there was no sign of methanol oxidation. Methanol oxidation in the cathode is an undesirable attribute for a direct methanol fuel cell, since methanol can pass through the membrane. Currently, direct methanol fuel cells lose efficiency from the direct oxidation of methanol over platinum in the cathode. Using alternative catalysts, such as the one shown in Figure 9 could therefore be a potential solution to the methanol crossover problem.

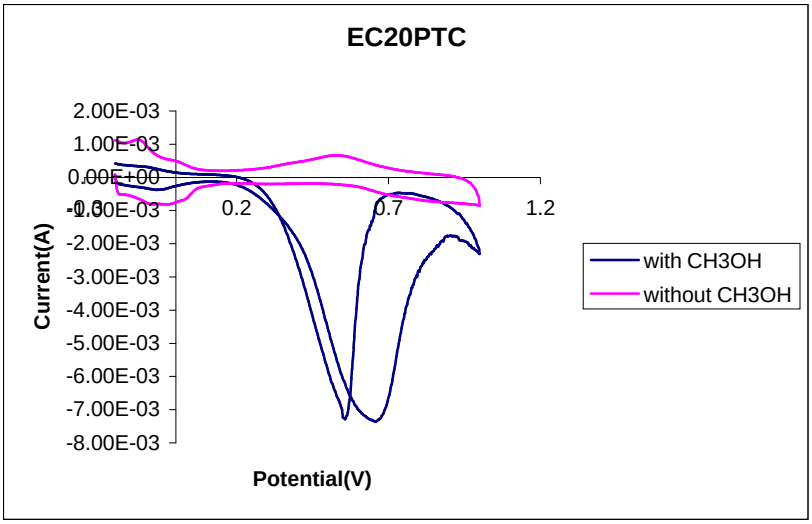


Figure 10. Methanol Oxidation Activity (platinum)

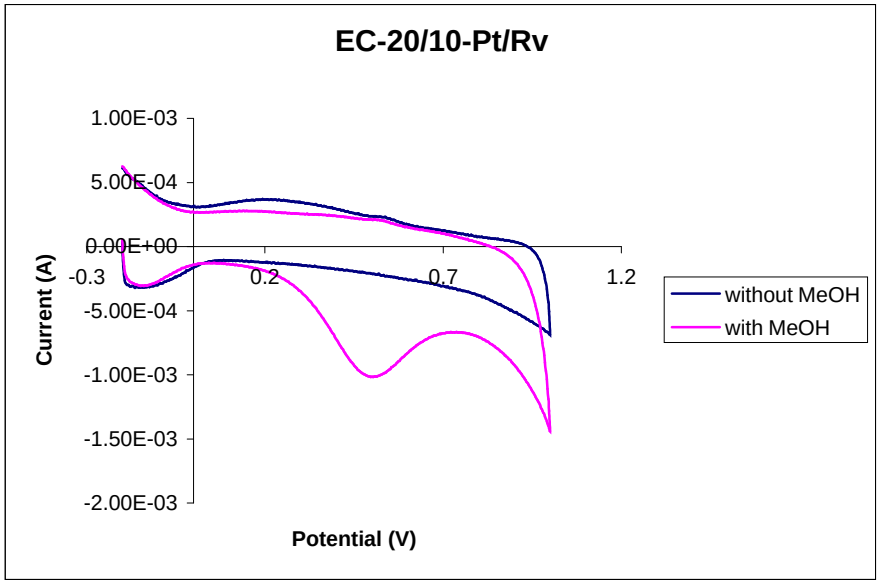


Figure 11. Methanol Oxidation Activity (platinum)

More activity quantitative measurements are in Table 1 below.

Table 1. Activity results

Activity of Samples		
samples	**page**	**activity mV**
Fe9(M) / PANI	92(3)	561.1
Fe9(M)/90(1) 75/25	11(M)	585
Fe9(M)/90(1) 50/50	11(M)	622
Fe9(M)/90(1) 25/75	11(M)	636
Fe31(E) - HF washed	31(E)	608.3
Co34(E)/CAN/KOH/HCl	34(E)	351
SiO2 - 900oC - washed	39(E)	660.1
Fe/SiO2 - 900oC - washed	44(E)	688.4
2Co/SiO2/900/washed	47(E)	667.2

The next step of this project was to measure the activity of different samples grown from Fe, Si, and Co. The most active samples were tested for activity, and from the result, further study was done. Figures 12 through 14 show the activity of three of the most active samples. Fe-SiO_2 44(E) has an activity of 615 mV, Fe2%-MgO 64(E) activity is 595, and MgO 76(E) has an activity of 412 mV. As shown by Table 2, these samples are not the most active of all the samples tested. However, when a separation testing was done (section 3.6) the catalyst separated into two layers showing that different types of fibers make up these samples**.** Appendix 1 contains the rest of the activity results.

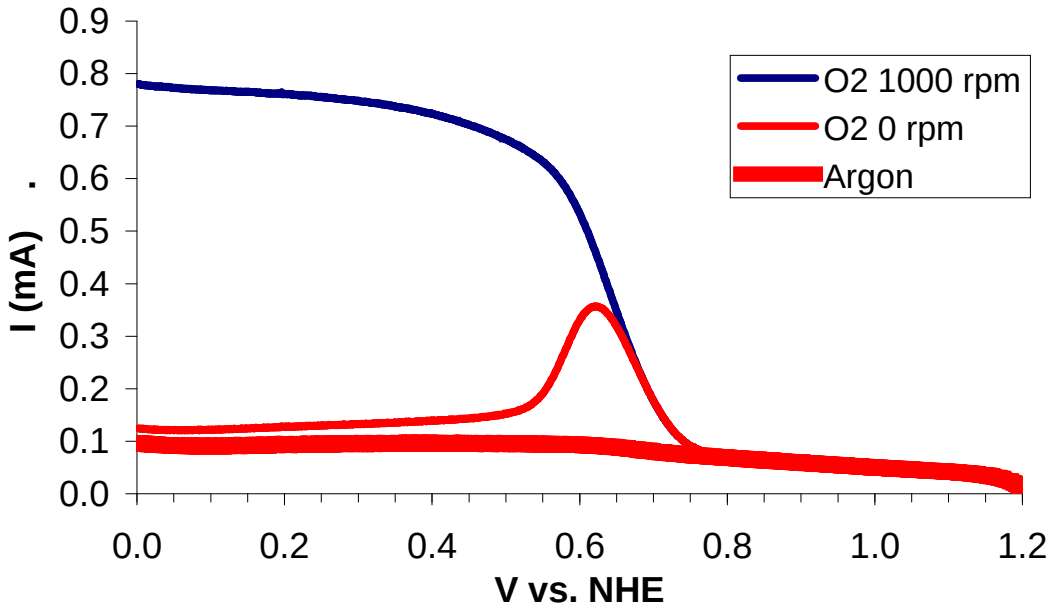


Figure 12. Fe-SiO_2 44(E) Activity

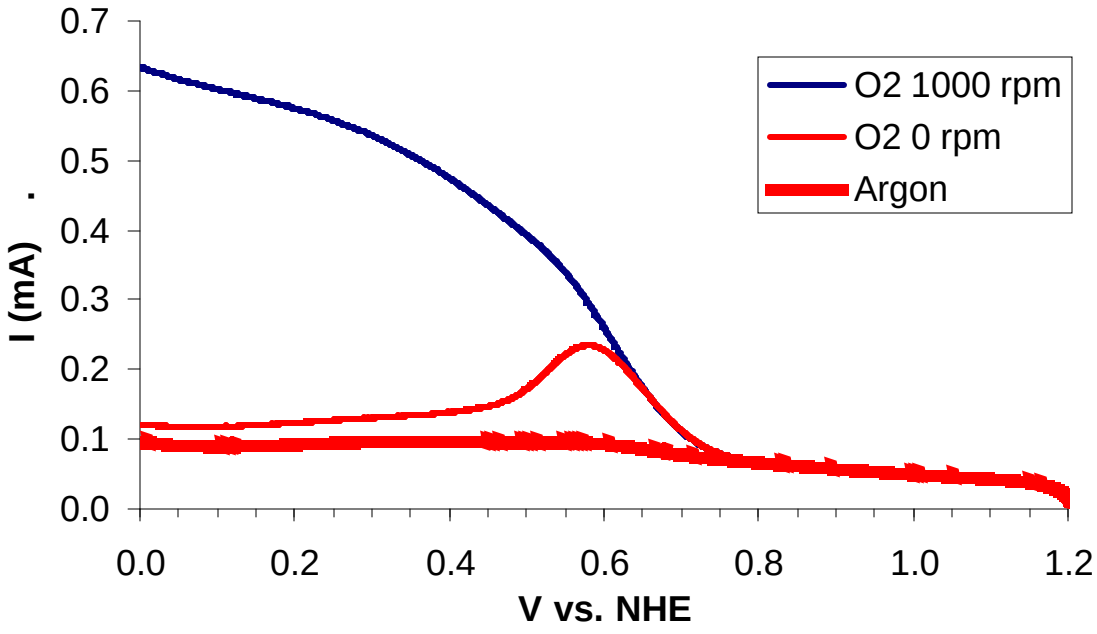


Figure 13. Fe2%-MgO 64(E) Activity.

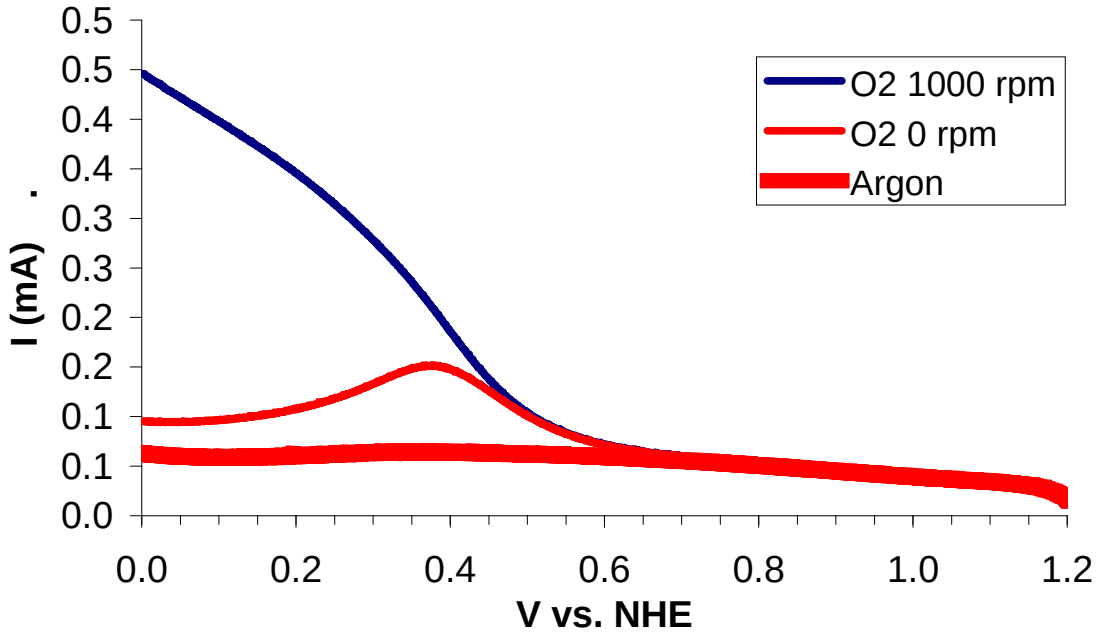


Figure 14. MgO 76(E) Activity

Table 2. Activity table

Name	Sample Used	Activity (mV)
O/SiO2/CH3CN/washed	39(E)	387
2%Fe/SiO2/HCl washed	44(E)	615
2%Co/SiO2/HCl washed	47(E)	526
2%Fe/Mg/ACN/HCl washed	64(E)	595
2%Co/MgO/HCl washed	66(E)	578
MgO/ACN/HCl	76(E)	412
Ni/Al2O3/CAN	22~	323
O/Al2O3/CH3CN	146~	490
2%Fe/Al2O3/CH3CN	3(EJB)	591

After performing hydrophobicity testing (section 3.6), and after separation of different types of carbons, some of the catalysts were tested for activity. Figure 15 shows the sample that was left after the extraction, and Figure 16 shows the sample that was extracted. The activities of both samples are different, the activity for the sample left is 505 mV and for the extract is 463 mV. Drawing conclusions from these figures, the

catalyst seems to be made of two different types of carbon with different activities. Figures 17 through 20 shows the activity for the other separated samples. The figures do not show a pronounced peak because the amount of sample used was very low. However, the activity could be measure by looking at the two different velocities of rotation and where they split. As shown in the explanation above the mass transfer effects of oxygen diffusion and the pure kinetic current effects are present when the electrode is rotating at higher speeds, while at no rotation only the mass transfer effects are present.

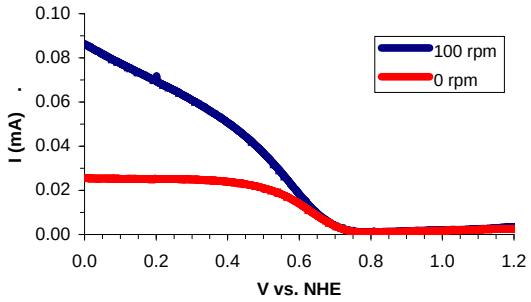


Figure 15. 44(E) bottom activity

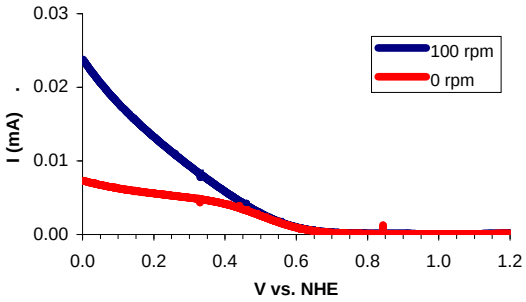


Figure 16. 44(E) wall activity

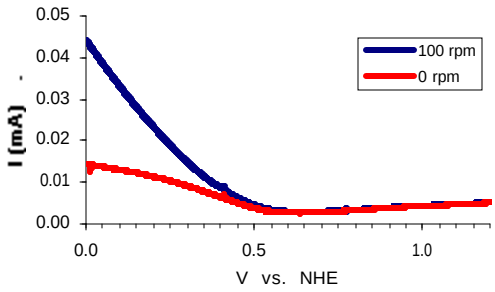


Figure 17. 64(E) bottom activity

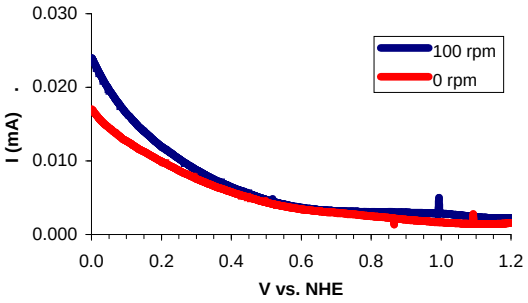


Figure 18. 64(E) wall activity

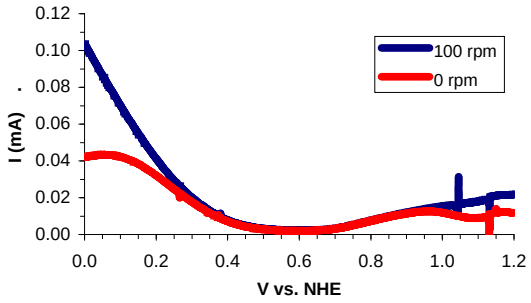


Figure 19. 76(E) bottom activity

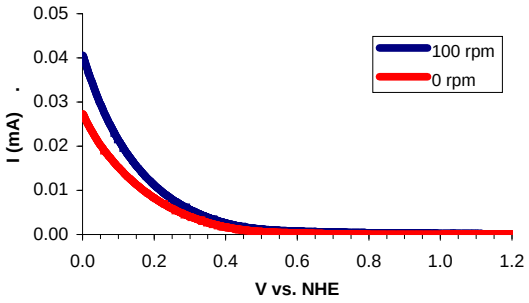


Figure 20. 76(E) wall activity

Table 3 summarizes activity results for the samples that had a separation when extraction was performed.

Table 3. Hydrophobicity Testing Activity

Hydrophobicity (Extraction) Testing Samples				
Name	**original sample**	**sample made**	**page**	**activity mV**
2%Fe/SiO2/HCl washed	44(E)	35(M) sample left at the bottom	44(M)	505
2%Fe/SiO2/HCl washed	44(E)	35(M) sample left at the wall	47(M)	463
2%Fe/Mg/ACN/HCl washed	64(E)	37(M) sample left at the bottom	45(M)	338
2%Fe/Mg/ACN/HCl washed	64(E)	37(M) sample left at the wall	48(M)	481
MgO/ACN/HCl	76(E)	39(M) sample left at the wall	49(M)	504
MgO/ACN/HCl	76(E)	39(M)sample left at the bottom	46(M)	301

4.3 Conductivity Testing

Conductivity was tested in order to determine the electrical resistance of the materials in a fuel cell environment. Conductivity for vulcan carbon is 71 S/m, for platinum is 44 S/m, and for active fibers is 53 S/m are taken as reference when determining how good the conductivity of a sample is. The polymer composite was tested for conductivity. However, its conductivity was very low, 17 S/m, when compared to the reference values. Figure 21 shows the resistance of the sample in three copper plates. The resistance was used to calculate the conductivity, and average conductivity was taken to be the final result for this sample.

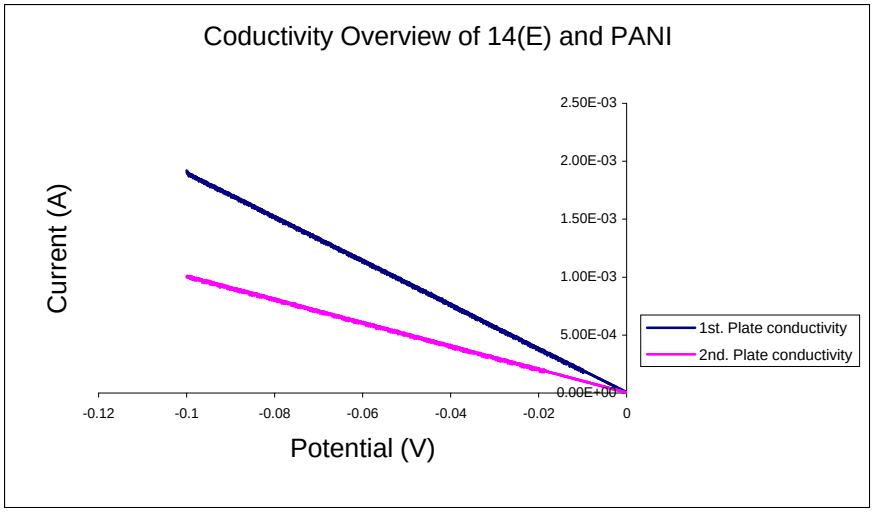


Figure 21. Conductivity of catalyst/PANI composite

Next, the conductivity for the dual catalyst samples was measured. Figure 22 shows the different conductivities obtained from the different amount of fibers in the samples.

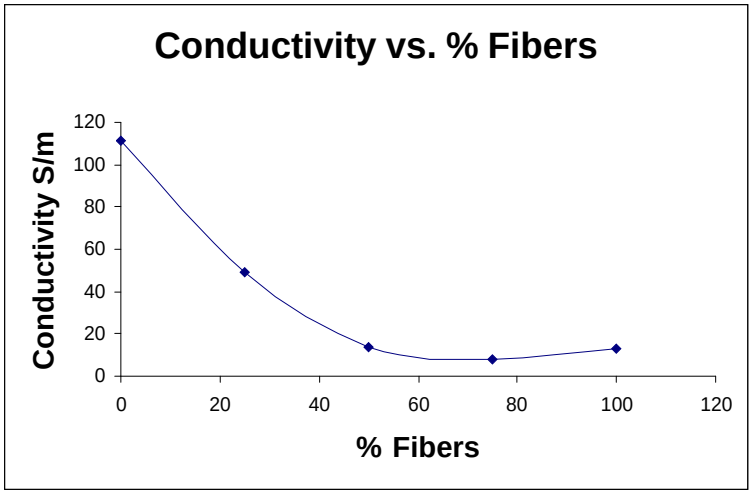


Figure 22. Conductivity vs. % of Fibers

From the study of these composites, it was determined that composites of highly active (but less conductive) and highly conductive (but less active) catalysts could be used to make better materials. The best composite was 25wt% fibers and the rest a secondary catalyst (9(M)/90(1)), and it was used to prepare a solution for fuel cell

elaboration and testing. Please refer to section 3.7 for more results. Table 4 shows quantitative conductivity results.

Table 4. Conductivity Results

Conductivity of Samples		
samples	**page**	**conductivity S/m**
Fe9(M) / PANI	92(3)	17
Fe9(M)/90(1) 75/25	11(M)	8
Fe9(M)/90(1) 50/50	11(M)	14
Fe9(M)/90(1) 25/75	11(M)	49
Fe31(E) - HF washed	31(E)	44
Co34(E)/CAN/KOH/HCl	34(E)	15
SiO2 - 900oC - washed	39(E)	4.3
Fe/SiO2 - 900oC - washed	44(E)	2
2Co/SiO2/900/washed	47(E)	25

Finally, conductivity for different Fe, Co, and Ni samples was measured to see which will give the highest value. Table 5 summarizes conductivity values for the samples described above, as well as, for the Fe, Co and Ni samples.

Table 5. Conductivity Results

Name	Sample Used	Conductivity S/m
O/SiO2/CH3CN/washed	39(E)	.2
2%Fe/SiO2/HCl washed	44(E)	11
2%Co/SiO2/HCl washed	47(E)	26
2%Fe/Mg/ACN/HCl washed	64(E)	32
2%Co/MgO/HCl washed	66(E)	1
MgO/ACN/HCl	76(E)	8
Ni/Al2O3/CAN	22~	16
2%Fe/Al2O3/CH3CN	3(EJB)	21

From the previous studies on activity and conductivity Fe and Co supported by SiO_2 or MgO gave high activity and better conductivity than fibers from Fe/Al_2O_3 in some cases.

4.4 Hydrophobicity Testing

Hydrophobicity was used as a separation method. The samples were dispersed in water and from their interaction with water some sample was dispersed and some was not. Hexane served as a solvent to separate the different types of carbon in order to determine whether different types of carbon nanofibers make up the catalyst, and how their structures affect the activity.

Hydrophobicity was first measured in pure Vulcan carbon, multiwall nanotubes samples, and stacked platelets commercial samples using toluene, chloroform and hexane as solvents to perform the organic extraction. Figure 23 shows the different samples and solvents, from the picture it can be seen that the stacked platelet carbon and the multiwall nanotubes are dispersed and forming a separate layer. These initial experiments demonstrated how different types of carbon could potentially be separated from one another by using organic extraction.

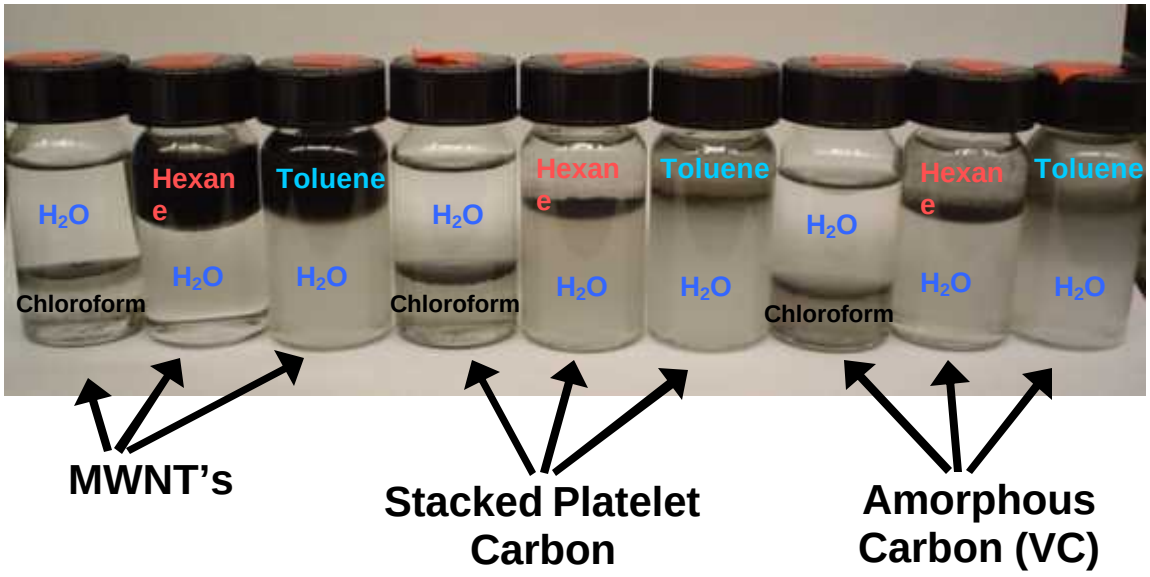


Figure 23. Hydrophobicity Testing

Different nitrogen-containing carbon samples were tested for hydrophobicity. The samples were separated with hexane, and two layers were formed. Extraction was performed with a pipet to separate the different types of carbon. Figure 24 shows the samples that were used.

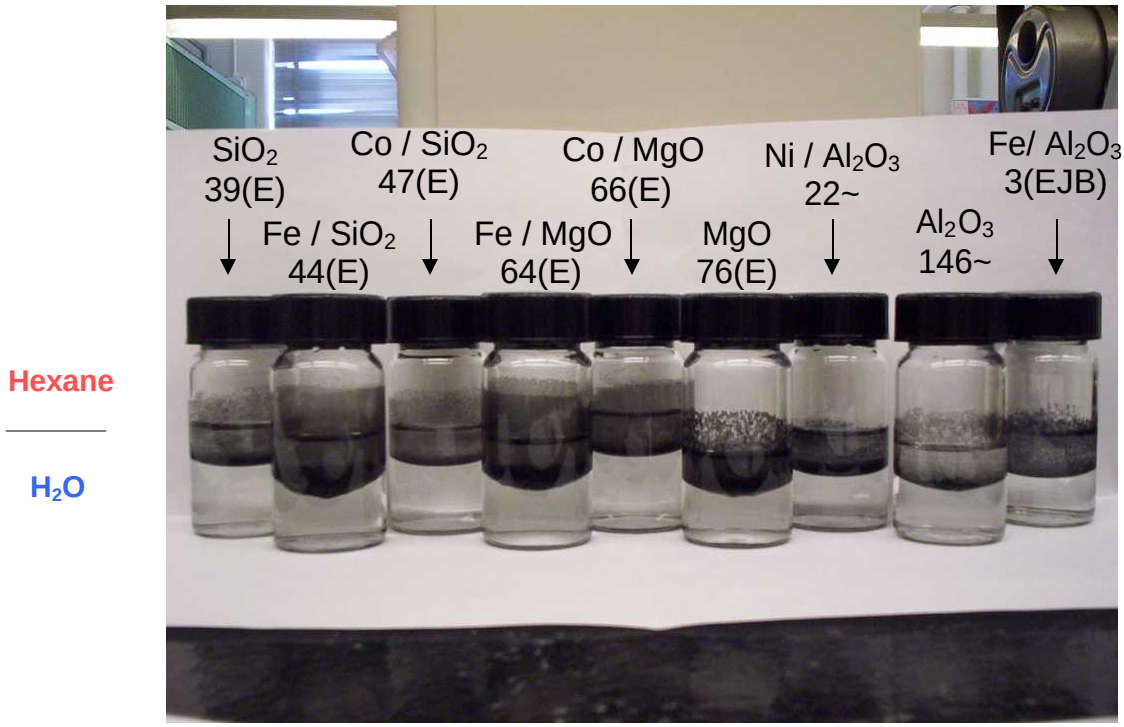


Figure 24. Hydrophobicity Testing

From the pictures displayed above, three samples that separated into two different layers were chosen to test for activity (shown in section 4.2) and the fibers were characterized using TEM (shown in section 4.5). The three samples are 44(E), 64(E), and 76(E). These samples were chosen according to the ratio of the carbon extracted vs. carbon left as Figure 25 shows. This figure shows that Fe samples have a high ratio of separation, as well as MgO samples.

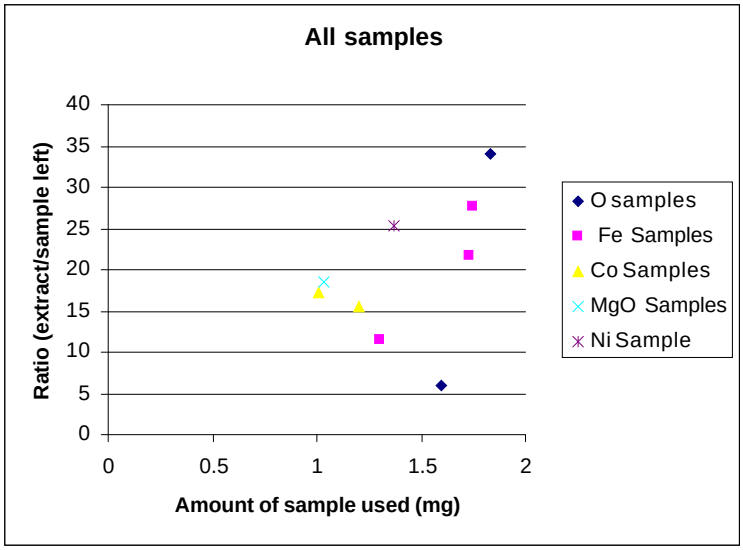


Figure 25. Ratio of extract: sample left

Figure 26 through 28 show the sample left in water, and the extract in hexane for three of the samples that showed separation.

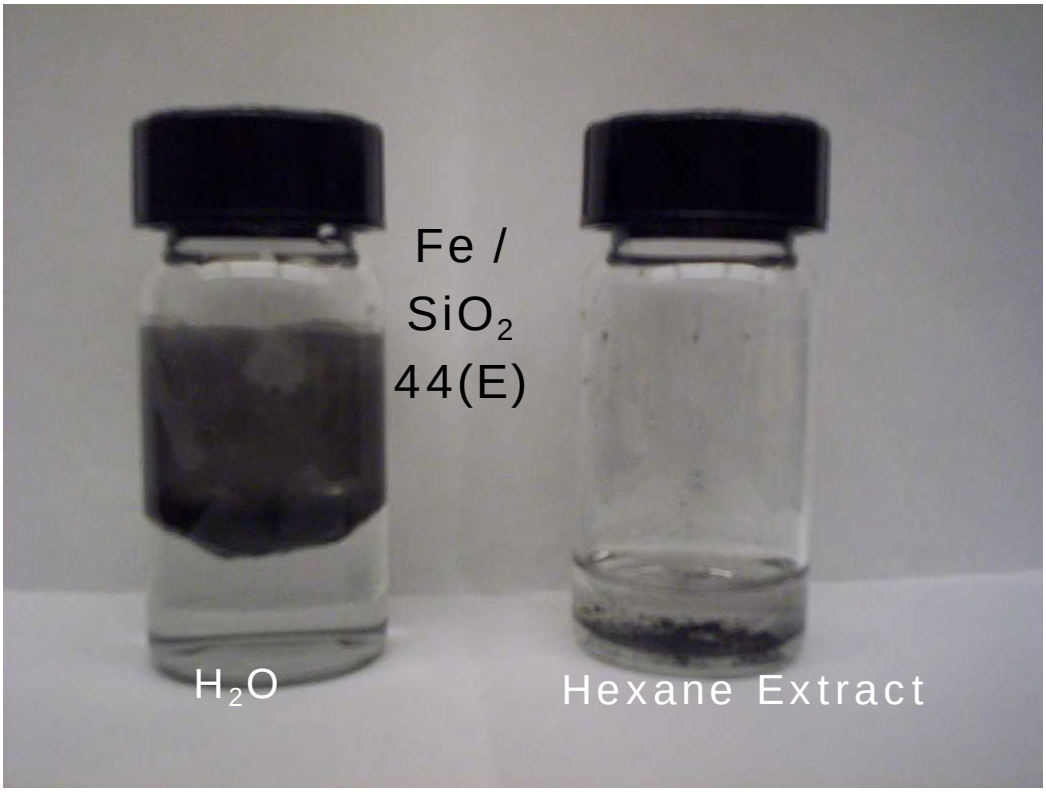


Figure 26. Fe/SiO_2 44(E) extraction

Figure 26 shows that Fe supported in Silica separated into two layers. The sample showed on the left vial is the sample that was left behind after extracting the organic layer with hexane. The sample on the right shows the sample extracted with hexane.

Figure 27. Fe/MgO 64(E) extraction

Figure 27 also shows the sample dispersed in water on the left. This is the sample that was left behind after extraction. On the right the vial contains the hexane extracted. These two samples were also analyzed to determine if they were different and the structure they possessed. Figure 28 shows the extraction for MgO, as described

previously the sample left is shown on the left, and the hexane extract on the right hand side.

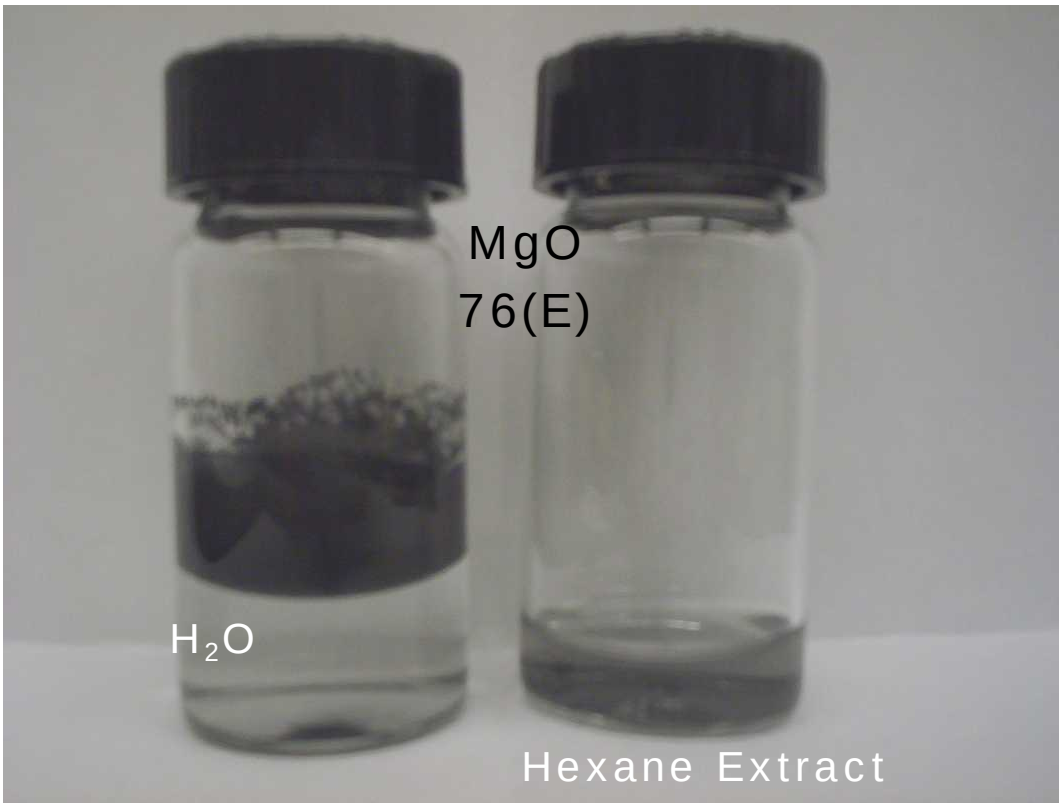


Figure 28. MgO 76(E) extraction

Table 6 summarizes the activity measurements taken for the samples above and the extracts. Activity graphs are shown in section 4.2 above, and in appendix 1

Table 6. Hydrophobicity Testing Activity

Hydrophobicity (Extraction) Testing Samples				
Name	**original sample**	**sample made**	**page**	**activity mV**
2%Fe/SiO2/HCl washed	44(E)	35(M) sample left at the bottom	44(M)	505
2%Fe/SiO2/HCl washed	44(E)	35(M) sample left at the wall	47(M)	463
2%Fe/Mg/ACN/HCl washed	64(E)	37(M) sample left at the bottom	45(M)	338
2%Fe/Mg/ACN/HCl washed	64(E)	37(M) sample left at the wall	48(M)	481
MgO/ACN/HCl	76(E)	39(M) sample left at the wall	49(M)	504
MgO/ACN/HCl	76(E)	39(M)sample left at the bottom	46(M)	301

4.4 TEM

TEM was used to determine the different types of fibers or compositions of the three samples separated in the hydrophobicity testing. As shown in the literature review, there are different types of carbon nanofibers structures. Figure 29 shows sample Fe-SiO_2 before it was separated with hexane. The figure shows that this sample is formed of stacked cup nanofibers with active edges; also it shows some solid fibers that influence the conductivity of the sample, as well as, some broken ladder fibers that could also help activity.

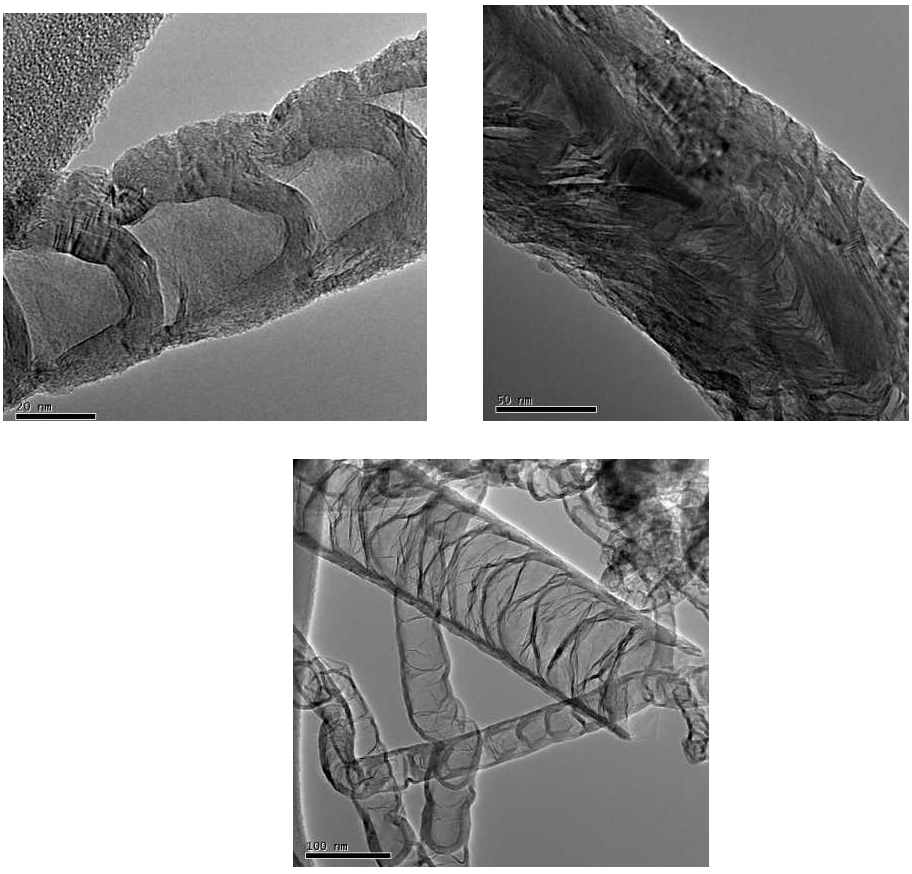


Figure 29. TEM Fe-SiO_2 44(E)

After the sample was separated as Figure 30 shows, the structure seems to be some amorphous carbon structure. Carbon nanofibers do not appear on the sample left after

separation. TEM characterization could not be done in the extract of the sample because of lack of sufficient sample; however, it could be that the extract was a different type of carbon that had the nanostructure showed for Figure 29.

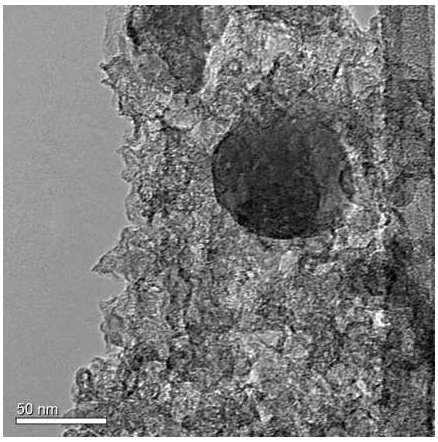
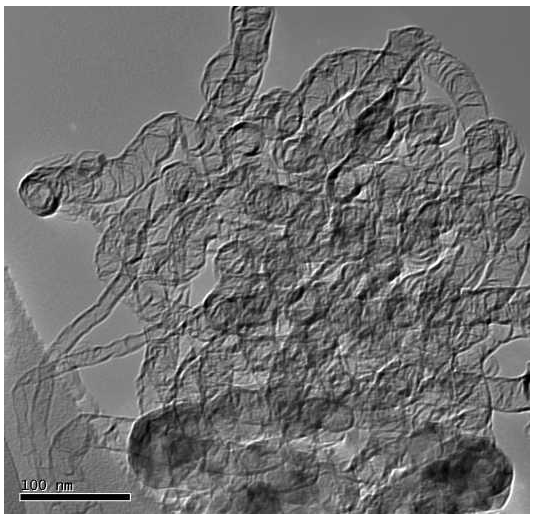
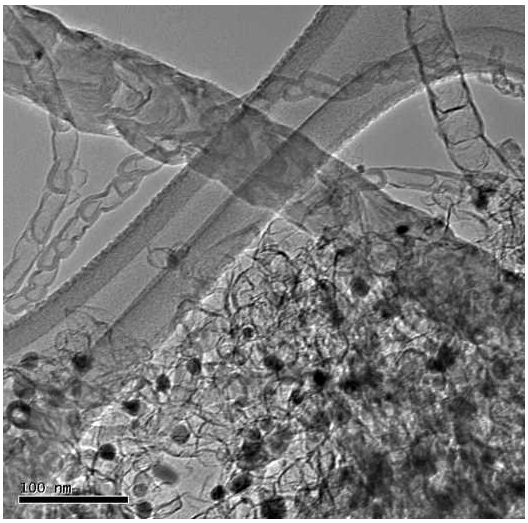


Figure 30. TEM Fe-SiO2 44(E) bottom

The structure of Fe/MgO 64(E) is shown in Figure 31. As shown in the pictures multiwall nanotubes, stacked cups, fibers, and some ladders form the structure of this sample. As explained in the sample before, the stacked cups, and the multiwall nanotubes will very much influence the activity and conductivity of the sample.





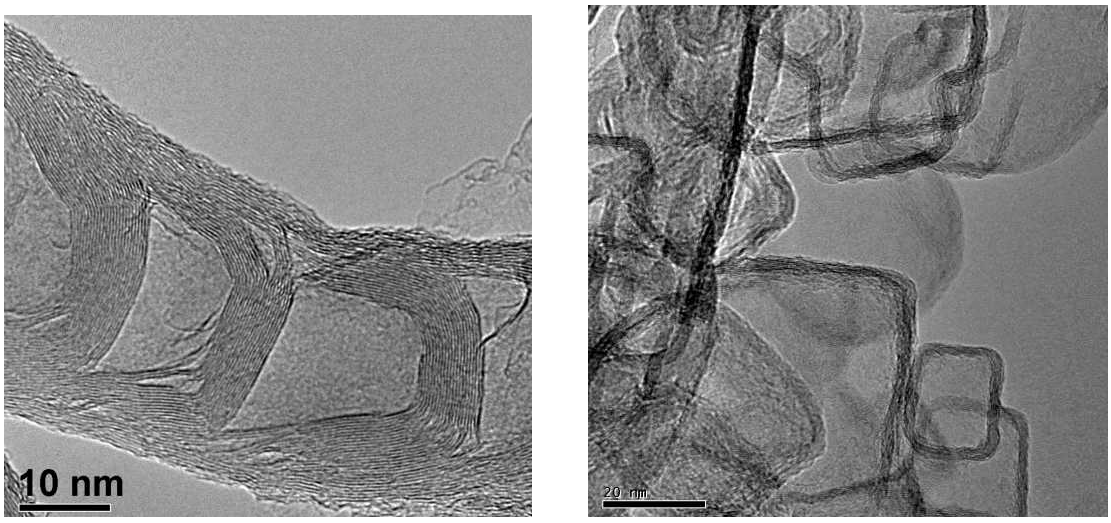


Figure 31. TEM Fe-MgO 64(E)

Figure 32 shows the sample left at the bottom of the vial after separation. The structure of these fibers is stacked cups. They are active fibers because of their edges they are able to reduce oxygen better.

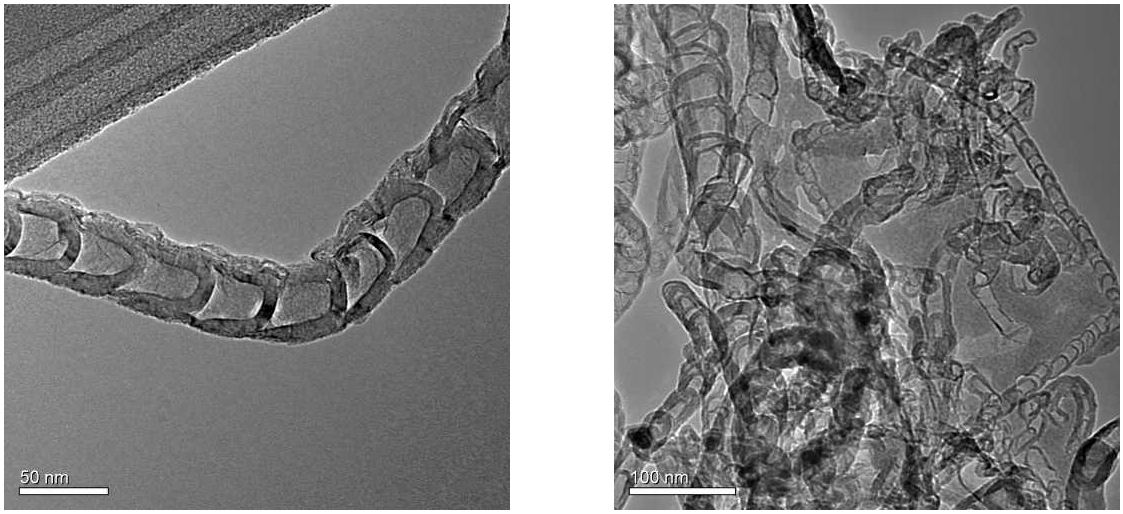
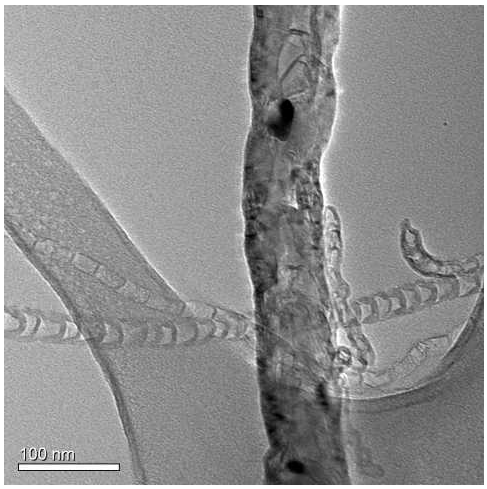
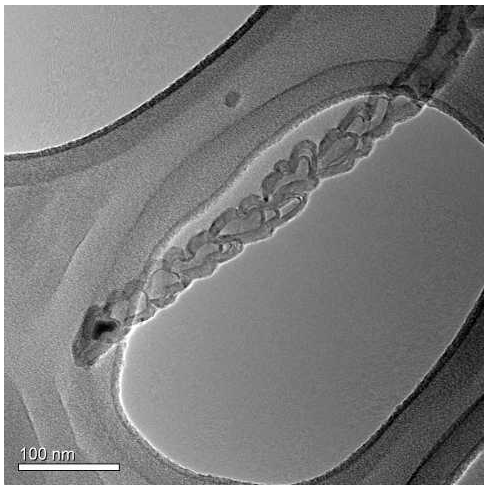
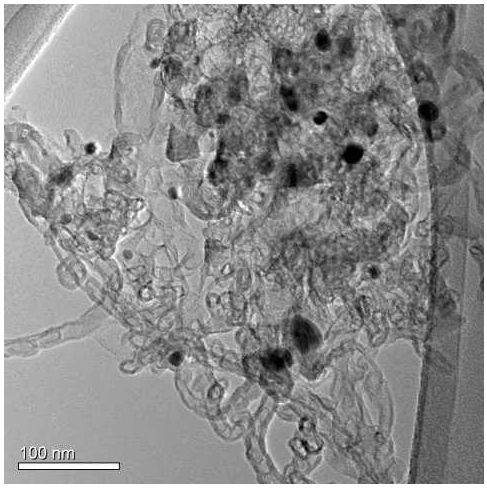


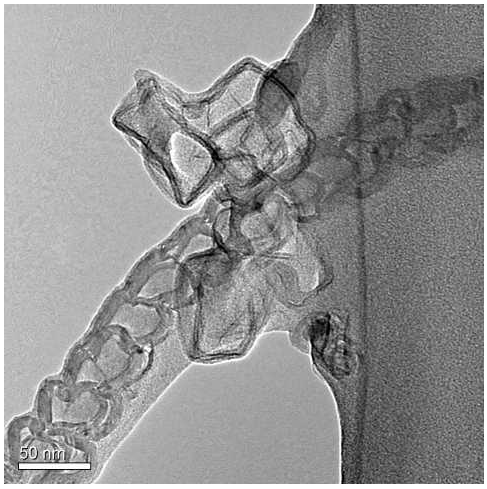
Figure 32. TEM Fe-MgO 64(E) bottom

Figure 33 shows the sample that was extracted with hexane. It shows stacked cups fibers, but also multiwall nanotubes. The stacked cups fibers will give more activity to the sample, and the nanotubes will make it more conductive.









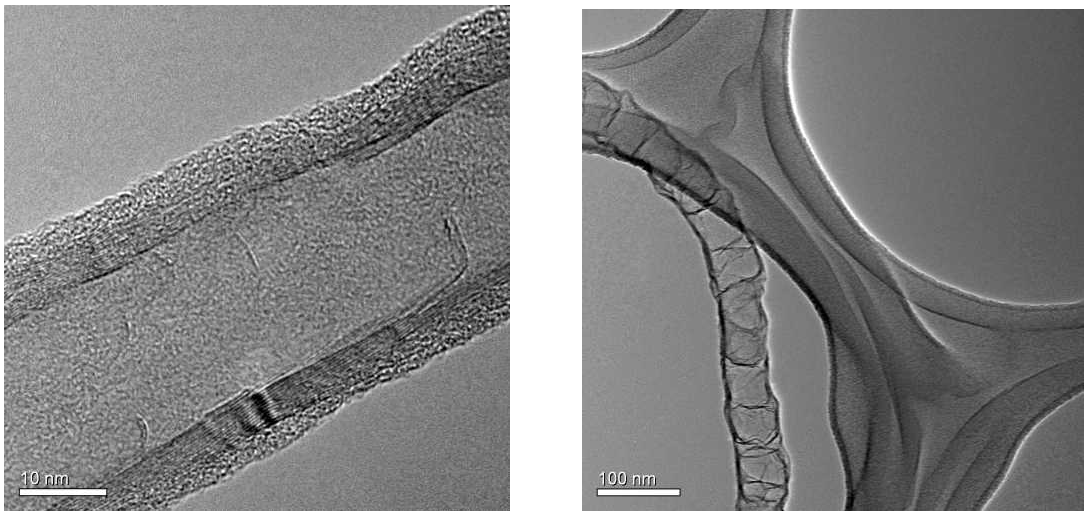


Figure 33. TEM Fe-MgO 64(E) wall.

Figure 34 shows the shape of carbon but not of fibers. The picture clearly shows that fibers did not grow. It makes sense because no metal was used in this sample.

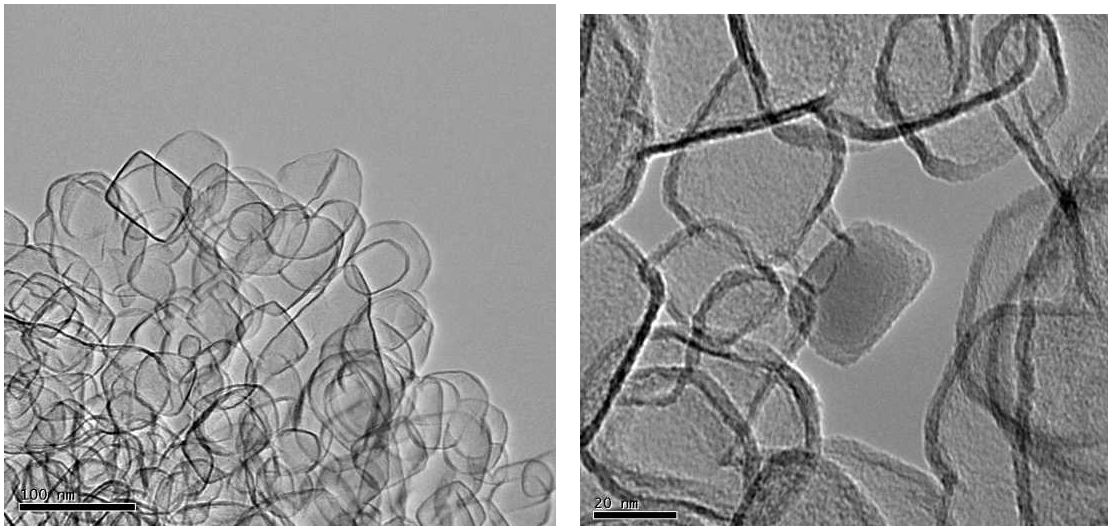


Figure 34. TEM MgO 76(E)

Figure 35 shows the sample left at the bottom of the vial after separation. The picture does not show any fibers.

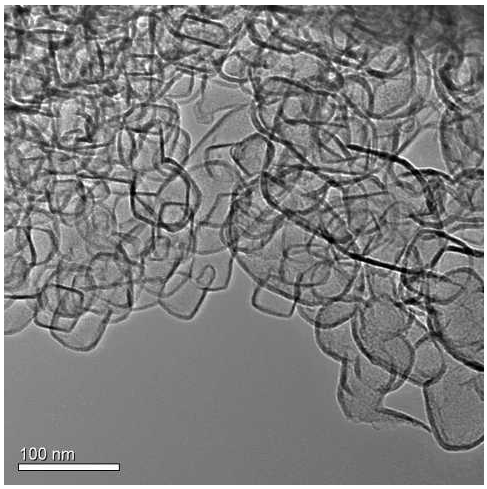


Figure 35. TEM MgO 76(E) bottom

Finally Figure 36 shows the extract from sample 76(E), no fibers are encounter in these pictures either.

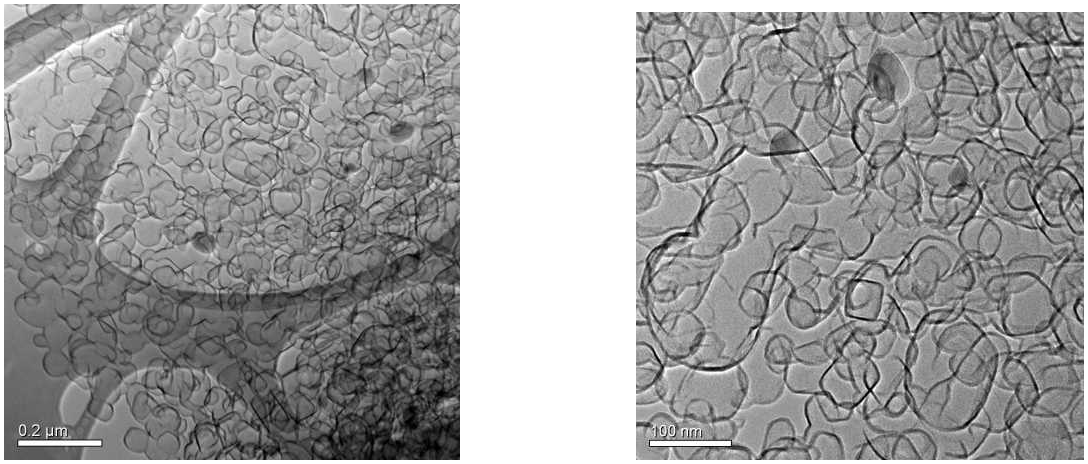


Figure 36. TEM MgO 76(E) wall

Table 7 shows the structure distribution of the different samples shown above. From this distribution is clear that fibers grown from Fe have more edge plane exposure because the majority of the fibers are of stacked cup shapes. In addition, fibers were not grown when there was no presence of a metal. For Fe-SiO_2 after performing the

extraction the two different layers showed different kind of fiber structure. In the Fe-MgO sample it also shows the split of nanofibers when the layers where separated. The sample left after extraction contains more stacked cup fibers, while the extract has multiwall nanotubes and solid fibers. Finally, for the MgO sample no fibers are present before or after separation.

Table 7. Structure Distribution

Sample	Stacked Cups	Fibers	MWNT's	Ladders
Fe / Al2O3	54%	10%	21%	15%
Ni / Al2O3	6%	17%	17%	60%
Fe / SiO2	71%	7%	18%	4%
Co / SiO2	66%	0%	13%	21%
Fe / MgO	42%	14%	9%	35%
Co / MgO	54%	10%	21%	15%

4.6 Fuel Cell Testing

Based on the results obtained for activity and conductivity, 25wt% fibers and the rest a secondary catalyst (9(M)/90(1)) was used to prepare a solution for fuel cell elaboration and testing. Testing was conducted at 20psi of Hydrogen and Oxygen pressure, at 140 degrees Celsius, and the open circuit voltage was .807 mV. Figure 37 below shows some of the results. As seen from the results, platinum still has a much better performance than the composite. At this point, research is focusing more on finding an adequate material for building MEA fuel cells, rather than making testing fuel cells. Considering the potential drop in region 1 is not severe this material has good activity. However, the conductivity and/or mass transfer is poor. This could be caused

by poorly connected electrodes. Work is underway to improve and optimize our preparation procedure.

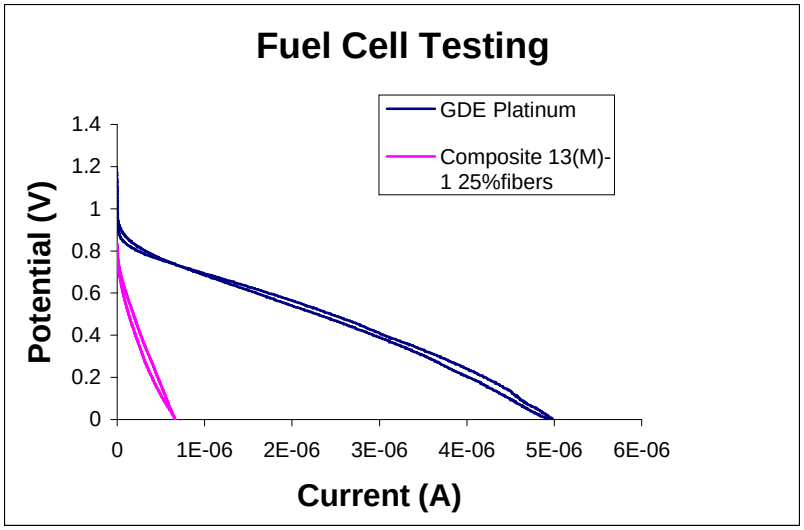


Figure 37. Fuel Cell Testing

5. Summary

Fuel cells are an alternative energy source to traditional energy sources. They create energy through the electrochemical reaction between hydrogen and oxygen, leaving water as a byproduct. Nitrogen containing carbon catalysts have been developed which make fuel cells more available and cheaper for manufacturing and commercialization.

In this study catalysts for the Oxygen Reduction Reaction (ORR) were prepared by the pyrolysis of acetonitrile over various supports. Different carbon catalysts have been developed using metals, in order to grow carbon nanofibers that will improve the activity and conductivity of the catalyst. Different experimental procedures have been used in order to characterize the catalyst, these procedures include: activity and conductivity testing, TEM, Hydrophobicity Testing, and Lab-scale Fuel Cell Testing. In this study, it was possible to separate different types of carbon using organic extraction, and the structure distribution was determined by using TEM characterization.

Nitrogen containing catalysts improved the activity of vulcan carbon from 30 mV to about 600 mV. Conductivity can be improved by making composite catalysts with a minimal effect on activity. Composites of highly active (but less conductive) and highly conductive (but less active) catalyst could be used to make better materials. Of these composites, the best was 25% active fibers and the rest a more conductive catalyst. Fe and Co supported by SiO_2 or MgO gave high activity and better conductivity than fibers from Fe/Al_2O_3 in some cases. Inactivity for methanol oxidation was confirmed, which is important for use in the cathode of methanol fuel cells. Activity and conductivity of some catalysts formed from Fe and supported on SiO_2 or MgO (activity of ~600 mV,

conductivity of ~30 S/cm) have similar properties as the commercial sample (activity ~750 mV, conductivity 44 S/m). Optimization of the preparation procedure could lead to better alternative cathode fuel cells.

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Appendix

Appendix 1.

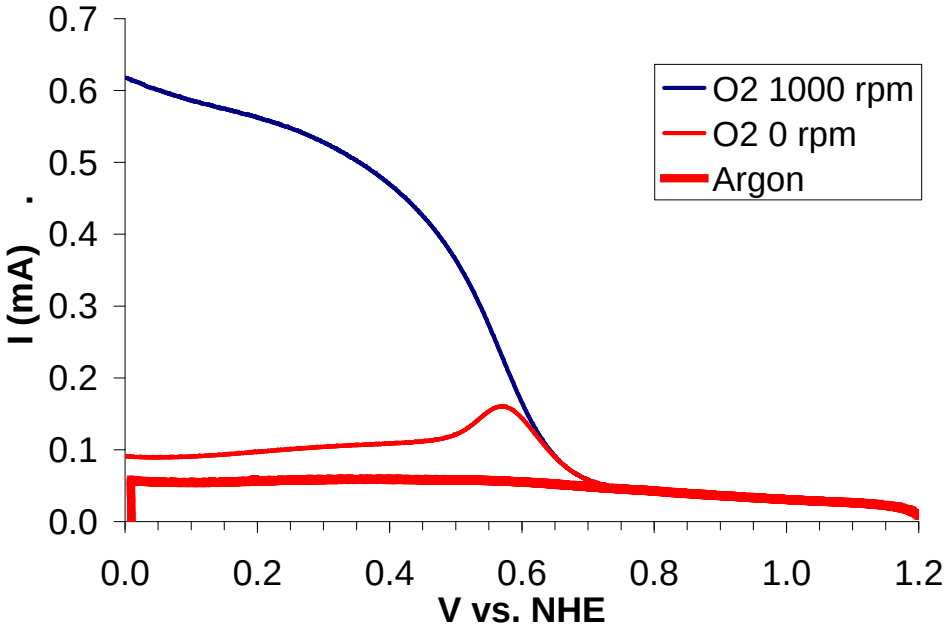

Figure 38. CO2%-MgO 66(E)

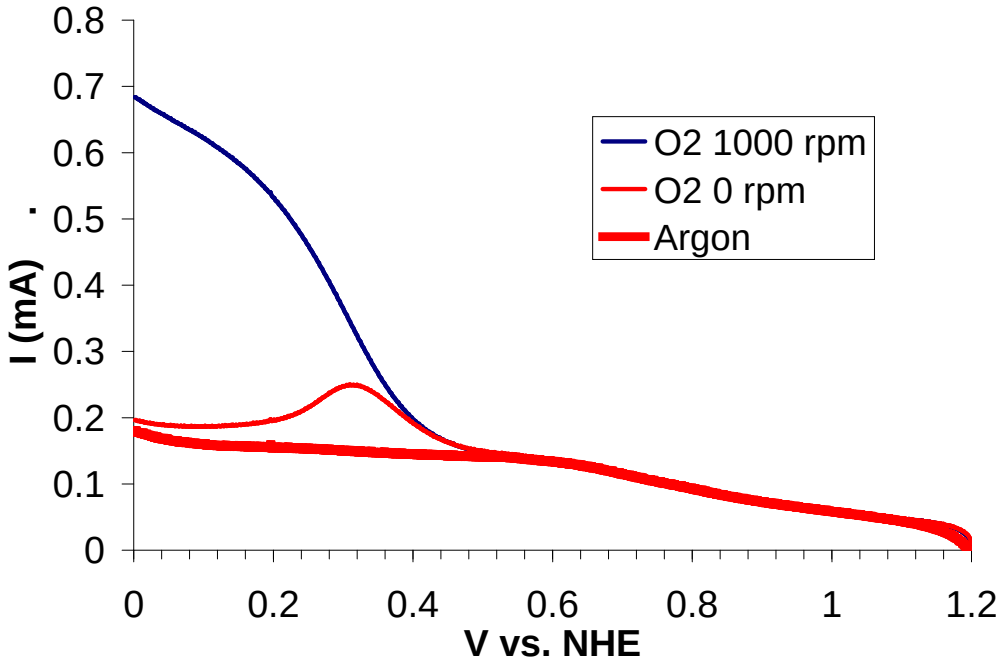

Figure 39. Ni-Al_2O_3 22(3)

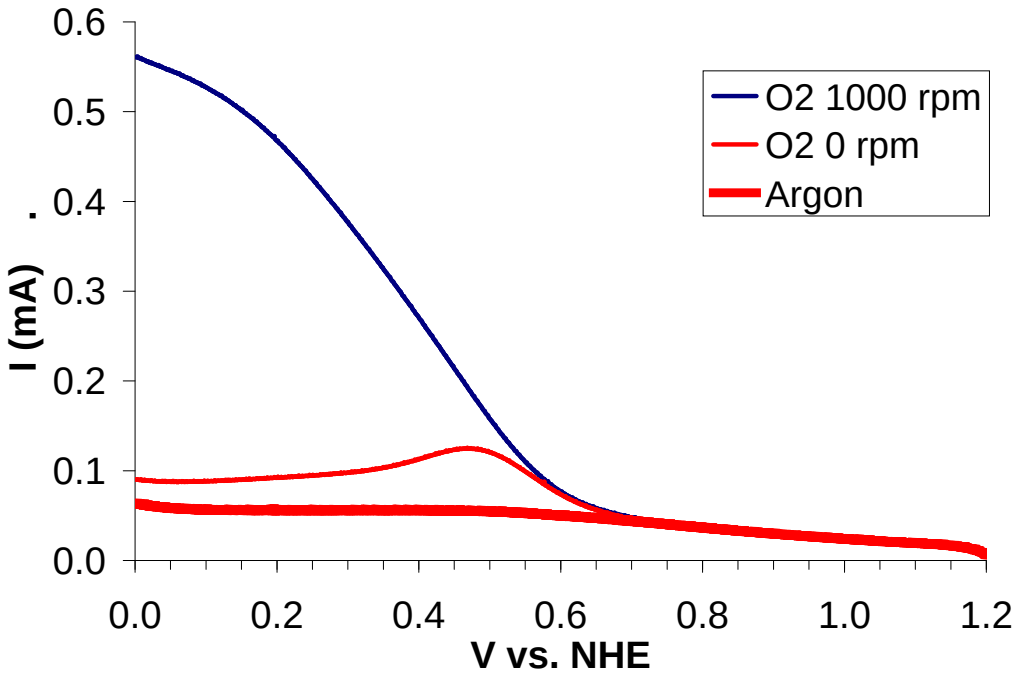

Figure 40. Al_2O_3 146(3)

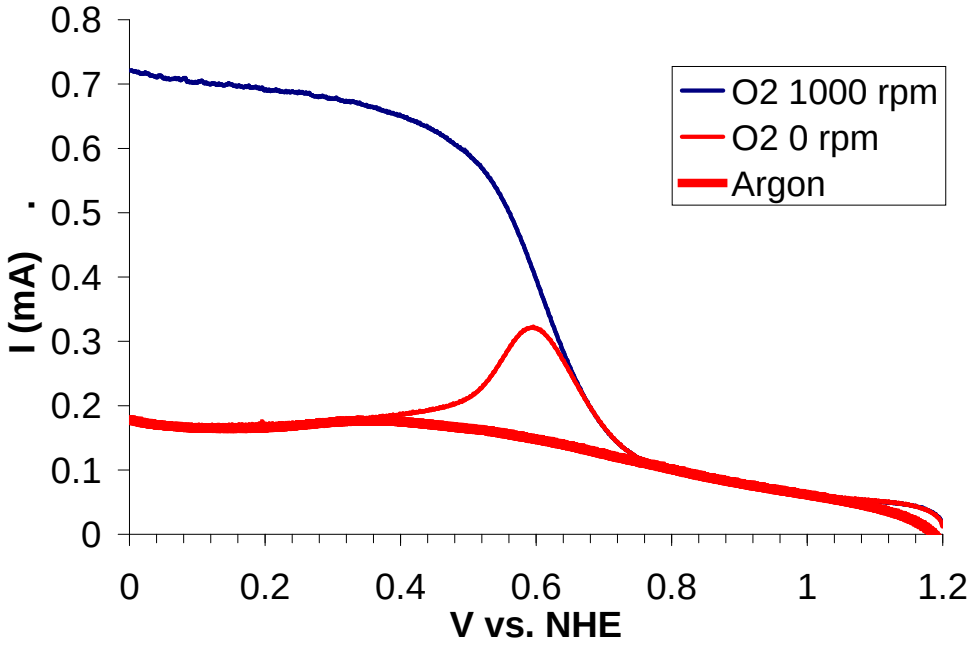

Figure 41. Fe-Al_2O_3 3(EJB)